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Dr. Robert J. Nowak

FINAL REPORT

Investigation of the interface between immiscible electrolytes  
applied to membrane electrochemistry

by

Petr Vanýsek

Northern Illinois University

Department of Chemistry  
DeKalb, IL 60115

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14 December 1994

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- The objective, approach and scientific conclusions:

The purpose of the work was to investigate various aspects of electrochemical and electrical behavior of interfaces between two immiscible solutions of electrolytes. These interfaces were either free standing, such as between immiscible liquid water and nitrobenzene, solidified, such as solution and a membrane, or semi-metallic, such as bathing solution surrounding the conducting polymer polyaniline. The interface has some properties similar to those of metal electrodes. Therefore, methodology known from the work with metal electrodes ("classical electrochemistry") can be applied to these studies in many cases.

We have used primarily cyclic voltammetry (i.e., current-voltage characterization) and impedance spectroscopy methods to observe the properties of the investigated interfaces. In a membrane composed of defined straight pores an anomalous conductivity of these pores was observed and studied in a detail. This phenomenon is known to be caused by the surface electroosmotic effect, but so far was seldom studied outside capillary electrophoresis. We believe that the phenomenon has importance in any microstructure carrying flux of electric charge.

A different type of membrane was that prepared from Nafion, a structured film of an ion exchanger. Ion transport through charged channels in a cast Nafion film was investigated to understand permeability to larger cations, such as  $\text{Zn}^{2+}$ . We found conditions when the zinc ion transport was suppressed, while overall high conductivity was retained. This may have importance in electrolyte separation in zinc storage battery industry. Rigorous treatment was used in the study of impedance properties of ionically/electronically conductive films made from polyaniline. A semiautomatic method to obtain and analyze impedance spectra was developed.

Since the major technique used was that of impedance spectroscopy, we have developed a table of simulated responses covering a number of possible evaluating methods. This helped tremendously in evaluating our own data and together with a chapter introduction to impedance, that I have written for the use of students in our laboratory, it will serve as a basis for planned monograph on impedance measurements.

A piezoelectric crystal, specifically designed for work in liquids, has been utilized to investigate interfacial tension and adsorption on a contact between two liquids. The preliminary work showed the viability of this approach. Currently (i.e., past the contract support) we are using a faster frequency counter and ability to custom make the sensing crystals to study systematically this new method. This project will result in a quality master thesis. A different technique, used in the earlier stages of our research, was based on a drop pressure measurement. The instrument and the method are still a stand-by, used during the quartz sensor work. The interfacial studies are essential tool for structure understanding because changes in interfacial tension are reflecting the state of charge on the interface which is, in turn, indicative of the interfacial structure itself.

Another pilot experiment to study changes on interfaces optically, using a probe-beam deflection method, was performed. It is ready to be continued when a suitable person becomes available.

The progress and the results of the work based on this contract were continuously documented by regular submission of Technical Reports. Overall, 18 reports were filed (see the list). The results of the work appeared in 13 publications.

The work, as a research on new initiative, has proven to be extremely successful. The phenomena associated with electrochemistry on L/L interfaces have caught attention of the scientific community. Increased number of publications related to these problems appear every year and international symposia on this subject are being organized. The Principal Investigator is routinely involved in co organizing such meeting forums. He has been also invited to write a monograph summarizing the state of art of the electrochemistry on liquid/liquid interfaces. The support of this area by the ONR contract has firmly placed roots and background for this discipline in the USA.

- Associates supported from the contract:

- Undergraduates

Dave Skotty (90-91)  
Dena Laval (91-92)  
Cynthia Pakus (91-93)  
Elise Brachtel (92-93)  
Brett Steigerwald (92-93)

- Graduate students

Alex Schreiner (90-91)  
Giselle Sandí (90-94)  
Denise Herrmann (91-93)  
Lizhuo Zhang (92-93)  
Simona Dragan (93-94)  
(currently a teaching assistant)

- Postdoctoral fellows

Antonín Trojánek (90-92)  
Ivan Krejčí (91-93)

- Publications:

- 1 Petr Vanýsek: Interfacial ion transport between immiscible liquids in: M. Blank and I. Vodyanoy (Eds.), *Membrane Electrochemistry, Advances in Chemistry Series Vol. 235*. p. 55. The American Chemical Society, Washington 1994.
- 2 Petr Vanýsek: Electrified Immiscible Liquid Boundaries: Conventional and Microscopic Interfaces. In: R. A. Mackay and J. Texter, Eds., *Electrochemistry in Colloids and Dispersions*, VCH Publishers, New York (1992), pp. 71-84.
- 3 Zdeněk Samec, Antonín Trojánek and Petr Vanýsek: Polarization phenomena at ionic membrane/electrolyte interfaces. A Nafion membrane between two electrolyte solutions. *J. Electroanal. Chem.* 332, 349-355 (1992).
- 4 Petr Vanýsek: Interfacial tension studies of electrified liquid/liquid interfaces: Classical techniques for new data. *Proceedings. The Electrochemical Society, Pennington, May 1993*.

- 5 Ivan Krejčí, Petr Vanýsek and Antonín Trojánek: Transport of  $\text{Zn}(\text{OH})_4^{2-}$  ions across a polyolefin microporous membrane. *J. Electrochem. Soc.* **14** (8), 2279–2283 (1993).
- 6 Giselle Sandí and Petr Vanýsek: Impedance and voltammetric studies of electrogenerated polyaniline conducting film. *Synthetic Metals* **64** (1994) 1–8.
- 7 Ivan Krejčí and Petr Vanýsek: Effect of zinc and iron ions on the electrochemistry of nickel oxide electrode: Slow cyclic voltammetry. *J. Power Sources* **47** (1–2), 79–88 (1994).
- 8 Petr Vanýsek: Analytical applications of electrified interfaces between two immiscible solutions. *TRAC – Trends in Analytical chemistry*, **12** (9), 357–363 (1993).
- 9 P. Vanýsek: Investigation of the interface between two immiscible electrolytes applied to membrane electrochemistry. Report. Gov. Rep. Announce. Ind. (U.S.), 91(20), Abstr. 154,618 (1991).
- 10 P. Vanýsek: Electrified microscopic and conventional interfaces between two immiscible solutions. Report. Gov. Rep. Announce. Ind. (U.S.), 91(20), Abstr. 158,285 (1991).
- 11 A. J. Zhang, V. I. Birss and P. Vanýsek: Impedance characterization of thin electrochemically formed palladium oxide films. *J. Electroanal. Chem.*, **378** (1/2) 63– (1994).
- 12 P. Vanýsek: Analytical applications of electrified interfaces between two immiscible solutions. Gov. Rep. Announce. Index (U.S.) 93(15), Abstr. No. 343,837 (1993).
- 13 P. Vanýsek, Charge transfer processes on liquid/liquid interfaces: The first hundred years. Gov. Rep. Announce. Index (U.S.) 93(11), Abstr. No. 331,409 (1993).

• Presentations:

P. Vanýsek: Low-frequency impedance studies on interfaces between two immiscible solutions of electrolytes. Pittsburgh Conference, Chicago, IL 4 March 1991. (Paper 052).

Antonín Trojánek and Petr Vanýsek: Polarization and resistance phenomena on Nafion thin film membranes. The Electrochemical Society meeting. Washington, DC., 10 May 1991.

David Skotty and Petr Vanýsek: Characterization of polymer coated electrodes by impedance spectroscopy and signal noise analysis. Graduate student symposium (Presentation by D. Skotty). Madison, WI, 17 May 1991.

P. Vanýsek, A. Trojánek, G. Sandí, A. F. Schreiner and D. R. Skotty: Charge transport studies on heterogeneous electrolyte interface: Voltammetric studies on interfaces of immiscible electrolytes. The ACS Central–Great Lakes Regional Meeting. Indianapolis, IN, 29 May 1991.

P. Vanýsek: Electrified immiscible liquid boundaries. ACS National Meeting. August 1991, New York.

Giselle Sandí and Petr Vanýsek: Impedance investigation of polyaniline conductive films. Poster session organized by AMOCO. Presented by G.S. 4 October 1991

P. Vanýsek: Electrochemical studies on the boundary of two immiscible solutions. Seminar, University of Wisconsin – Madison, 17 October 1991.

P. Vanýsek: Ion Transport Through Nafion Films. MUACC, Ann Arbor, MI., 25 October 1991.

P. Vanýsek: Electrochemical studies of the boundary of two immiscible solutions. Seminar, Loras College, Dubuque, IA, 5 November 1991.

P. Vanýsek and I. Krejčí: Interfacial tension studies of interfaces between two immiscible electrolyte solutions. The Pittsburgh Conference. New Orleans, LA, March 13, 1992. Paper # 1259.

I. Krejčí and P. Vanýsek: Effect of applied electrical potential on interfaces between two immiscible electrolytes. ECS Graduate student symposium, DeKalb, IL 3 April 1992. (By IK)

G. Sandí and P. Vanýsek: Impedance studies of acid environment of poly(aniline) films electrochemically deposited on platinum electrodes. ECS Graduate student symposium, DeKalb, IL 3 April 1992. (By GS)

P. Vanýsek and G. Sandí: Impedance and voltammetric characterization of electrochemically deposited poly(aniline) conducting films. The Electrochemical Society spring meeting. San Louis, MO, 18 May 1992, Paper #452. (By GS).

I. Krejčí and P. Vanýsek: Transport of  $\text{Zn}(\text{OH})_4^{2-}$  ions across polyolefin microporous membranes. The Great Lakes Regional ACS meeting, Milwaukee, WI, 1–3 June 1992. (By IK)

G. Sandí and P. Vanýsek: Impedance of poly(aniline) films electrochemically deposited from acid media. The Great Lakes Regional ACS meeting, Milwaukee, WI, 1–3 June 1992. (By GS)

P. Vanýsek: Charge transfer processes of liquid/liquid interfaces: First hundred years. The Electrochemical Society Meeting, Toronto, Canada, 11–16 October 1992, Paper # 667.

P. Vanýsek, Z. Samec and A. Trojánek: Polarization phenomena at the interface between ionic membrane/electrolyte: A Nafion membrane between two electrolyte solutions. The Electrochemical Society Meeting, Toronto, Canada, 11–16 October 1992, Paper # 676.

I. Krejčí and P. Vanýsek: Interfacial tension studies on liquid/liquid interfaces using a bubble pressure method. The Electrochemical Society Meeting, Toronto, Canada, 11–16 October 1992, Paper # 682. (By IK)

P. Vanýsek: Potentiometric and amperometric detection on liquid/liquid interfaces. Workshop on chemical sensors, Chicago Section of the Electrochemical Society, October 30, 1992.

G. Sandí and P. Vanýsek: Impedance investigation of ion transport through Nuclepore membranes. A poster. Chicago Section of the Electrochemical Society, October 30, 1992. (By GS).

P. Vanýsek: Electrified interfaces between immiscible ionic solutions: Interfacial tension and related phenomena. The Pittsburgh Conference. 9 March 1993, Paper 386.

G. Sandí and P. Vanýsek: Impedance and SEM studies of ion transport across Nuclepore membranes. The Southern Wisconsin and Chicago Sections of the Electrochemical Society, Graduate Student Symposium, Milwaukee, 16 April 1993. Presented by GS.

Petr Vanýsek: Interfacial tension studies of electrified liquid/liquid interfaces: Classical techniques for new data. The Electrochemical Society meeting, Honolulu, 18 May 1993.

G. Sandí and Petr Vanýsek — Impedance spectroscopy studies of ion transport across polycarbonate membranes modified with ion exchanger. Pittcon 1994, paper 208, 28 February 1994. (by GS).

- List of technical reports:

ONR Technical Report No. 040: Petr Vanýsek: Electrified microscopic and conventional interfaces between two immiscible electrolyte solutions. Progress report. 24 June 1991.

ONR Technical Report No. 041: Antonín Trojánek and Petr Vanýsek: Resistance phenomena accompanying alkali metal cation migration through a Nafion thin film membrane. Progress report. 15 August 1991.

ONR Technical Report No. 042: Petr Vanýsek: Interfacial ion transport between immiscible liquids. Accepted manuscript for ACS Advances in Chemistry Series, No. 235. 24 June 1992.

ONR Technical Report No. 043: Petr Vanýsek: Electrified immiscible liquid boundaries: Conventional and microscopic interfaces. Published chapter in Electrochemistry in Colloids and Dispersions. VCH Publishers, New York 1992. 26 June 1992.

ONR Technical Report No. 044: Z. Samec, A. Trojánek and P. Vanýsek: Polarization phenomena at ionic membrane/electrolyte interfaces. A Nafion membrane between two electrolyte solutions. Published article in J. Electroanal. Chem. 332 (1992) 349. 15 September 1992.

ONR Technical Report No. 045: Petr Vanýsek: Interfacial tension studies of electrified liquid/liquid interfaces: Classical techniques for new data. A manuscript for ECS Proceedings of the Society meeting in spring 1993. 14 December 1992.



ONR Technical Report No. 046: G. Sandí and P. Vanýsek: Impedance and voltammetric studies of electrogenerated polyaniline conducting films. Submitted manuscript to Synthetic Metals. 14 December 1992.

ONR Technical Report No. 047: I. Krejčí, P. Vanýsek and A. Trojánek: Transport of  $\text{Zn}(\text{OH})_4^{2-}$  ions across a polyolefin microporous membrane. Submitted manuscript to J. Electrochem. Soc. 22 December 1992.

ONR Technical Report No. 048: Petr Vanýsek: Charge transfer processes on liquid/liquid interfaces: The first hundred years. Submitted manuscript to the Journal of the Electrochemical Society. 30 December 1992.

ONR Technical Report No. 049: I. Krejčí and P. Vanýsek: Effect of zinc and iron ions on the electrochemistry of nickel oxide electrode: Slow cyclic voltammetry. Submitted manuscript to the Journal of Power Sources. 7 April 1993.

ONR Technical Report No. 050: I. Krejčí, P. Vanýsek and A. Trojánek: Transport of  $\text{Zn}(\text{OH})_4^{2-}$  ions across a polyolefin microporous membrane. Revised manuscript for J. Electrochem. Soc. 7 April 1993.

ONR Technical Report No. 051: P. Vanýsek: Analytical applications of electrified interfaces between two immiscible solutions. Submitted manuscript to the Trends in Analytical Chemistry. 7 April 1993.

ONR Technical Report No. 052: I. Krejčí, P. Vanýsek and A. Trojánek: Transport of  $\text{Zn}(\text{OH})_4^{2-}$  ions across a polyolefin microporous membrane. Published article in J. Electrochem. Soc. 20 July 1993.

ONR Technical Report No. 053: P. Vanýsek: Analytical applications of electrified interfaces between two immiscible solutions. Published article in the Trends in Analytical Chemistry. 10 January 1994.

ONR Technical Report No. 054: P. Vanýsek: Introduction to electrochemical impedance. A laboratory instruction guide. 2 March 1994.

ONR Technical Report No. 055: I. Krejčí and P. Vanýsek: Effect of zinc and iron ions on the electrochemistry of nickel oxide electrode: Slow cyclic voltammetry. Published article in the Journal of Power Sources. 12 March 1994.

ONR Technical Report No. 056: A. J. Zhang, V. I. Birss and P. Vanýsek: Impedance characterization of thin electrochemically formed palladium oxide films. Submitted manuscript to the Journal of Electroanalytical Chemistry. 23 March 1994.

ONR Technical Report No. 057: Charge transfer processes of liquid/liquid interfaces: The status in 1994. Submitted manuscript to the Electrochimica Acta. 12 September 1994.

- Transitions:

The investigation of the electrochemical aspects of the liquid/liquid interfaces has resulted in a number of collaborations throughout the world. The closest to home is an ongoing research collaboration with Dr. R. Corn at the University of Wisconsin—Madison. His work centers on the second harmonic generation on liquid/liquid interfaces. Our contribution has been assistance with the electrochemical nature of the instrumental arrangement. Involved collaboration now exists with the research group of Prof. V. I. Birss at the University of Calgary. Our contribution was transfer of experimental methodology (i.e., impedance studies) to their metal oxide studies. The structure of metal oxides is more remote from the liquid/liquid interests, but it is closely related to general nanostructures of surfaces. And in particular, their thorough work on polyaniline impedance investigation is an extension of our own work. Initiated collaboration with the Institut of Bio- und Chemo-sensorik in Münster, Germany promises to continue our efforts in microinterface investigation, applied to analytical purpose. The actual transition to a government research effort is our collaboration with DoE, Argonne National Laboratory. Here we were invited to collaborate on designing an experiment involving X-ray reflectivity studies on liquid/liquid interfaces. The purpose of this work is to probe the structure of an interface between two immiscible liquids, while modifying its structure electrochemically. Although so far the support for this project was not granted by the ONR, we are continuing with our plans to go ahead with the work and seek support, if necessary, elsewhere.

- Highlights of selected publications:

(2) This chapter introduces the most important achievement in the electroanalytical applications of the liquid/liquid interface, the utilization of the so-called microinterface. In a phenomenon similar to that of microelectrodes with dimension similar to the thickness of the diffusion layer, relative decrease in resistance and charging current is observed. This allows increased detection in analytical applications as well as maintaining steady-state current in amperometric applications.

(7) This paper is particularly important in introducing very slow (0.05 mV/s) voltammetry to the study of porous systems. The extremely slow scan allows the investigate the inner regions of porous micro and nano structures, rather than just the surface in contact with the bulk solution. Our work investigated sintered porous nickel oxide material, but can be applied to other porous systems.

(6) This is our contribution to the large volume of work on polyaniline films. We have concentrated on impedance investigation of very thin polyaniline films, to learn more about the nature of the film during its oxidation/reduction transition. Impedance on thin films, although more difficult to do, is easier to interpret. Unlike the thick films, that often require implementation of the distributed element concept, the thin films can often be modeled by discrete components.

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